Applications of Cellulose Conversion Technology to Ethanol Production from Corn

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Abstract

Cellulosic biomass includes agricultural and forestry wastes, municipal solid waste, and energy crops. Enough ethanol could be made from cellulosic biomass within the United States to replace all gasoline, reducing our strategic vulnerability and lowering our trade deficit for imports. Ethanol blends and neat fuel also decrease emissions of carbon monoxide and smog-forming compounds, respectively. In addition, producing ethanol from biomass does not contribute to the accumulation of carbon dioxide in the atmosphere and the potential for global climate change. The simultaneous saccharification and fermentation (SSF) process is favored for producing ethanol from the major fraction of biomass, cellulose, because of its low cost potential. Technology has also been developed for converting the second largest fraction, hemicellulose, into ethanol. The remaining fraction, lignin, can be burned as boiler fuel to power the conversion process and generate extra electricity to export. Developments in conversion technology have reduced the selling price of ethanol from about $3.60/gal 10 years ago to only about $1.27/gal now. Additional technical targets have been identified to bring the selling price down to about $0.67/gal, a level that is competitive with gasoline from oil at $25/bbl. However, ethanol could be produced at prices similar to ethanol from corn if low-cost feedstocks are used. In particular, conversion of the fiber in corn to ethanol could increase plant revenues for this fuel while increasing the protein content and unit price of animal feed coproducts.

Introduction

Transportation fuels are almost totally derived from petroleum and account for more than one-quarter of the total energy used in the United States in 1989, more than 81 quads (U.S. Department of Energy 1990). Currently, about 50% of all petroleum used in the United States is imported from other countries, and imports have risen markedly over the last few years (U.S. Department of Energy 1990). Because OPEC controls about 75% of the world's oil reserves, while the United States has only about 5% of that total, it is likely that petroleum imports will continue to rise. Few substitutes currently exist for petroleum-based transportation fuels, and the United States is extremely vulnerable both strategically and economically to disruptions in their supply, as shown by our experience with Iraq's invasion of Kuwait. Shortages of transportation fuels previously triggered the "energy crisis" of 1973 and subsequent events. In addition, imported petroleum contributed about 40% of the balance-of-payments deficit for the United States in 1989 (Wald 1990).

Many cities, such as Los Angeles, suffer from poor air quality because of smog caused primarily by evaporative losses during fueling of automobiles, losses from the fuel system, and nitrogen oxides and unburned hydrocarbons from automotive exhaust (U.S. Environmental Protection Agency 1989). Other high-altitude cities, such as Denver, experience excessive levels of carbon monoxide because of incomplete combustion of carbon-containing fuels. Petroleum-derived transportation fuels are the source of up to two-thirds of carbon monoxide and one-third to one-half of smog-causing emissions (U.S. Environmental Protection Agency 1987; Browning et al. 1981; Risch 1988; U.S. Department of Energy 1978; Wilson 1987).

Scientists predict that the accumulation of carbon dioxide in the atmosphere as we burn fossil fuels could trap heat and cause global climate change. Possible consequences of this "greenhouse effect" include transformation of huge areas of our country from heavily forested woodlands (the Southeast) into deserts and movement of the corn belt from the Midwest to Canada over the next 40 to 50 years. The United States is responsible for about one-quarter of the carbon dioxide released into the atmosphere from fossil fuel use, and transportation fuels produced from petroleum contribute about 27% of that total (Edmonds et al. 1989).

Ethanol is a clean-burning liquid fuel that can be readily substituted for gasoline in our transportation sector. When ethanol is produced from renewable sources of cellulosic biomass, ethanol use can improve energy security, reduce the balance-of-payments deficit, decrease urban air pollution, and reduce the accumulation of carbon dioxide (Wyman and Hinman 1990; Lynd 1989; Lynd 1990; Lynd et al. 1991). The Ethanol from Biomass Program, managed by the National Renewable Energy Laboratory (NREL) for the Department of Energy (DOE), is directed at lowering the cost of ethanol production to the point at which ethanol can compete with gasoline without tax incentives, so that the benefits of this unique fuel can be realized. In this overview, the benefits of ethanol use will be briefly summarized, and the technology for ethanol production from cellulosic biomass will be described. Opportunities for applying this technology to increase revenues from dry and wet milling processes for ethanol production from corn will be discussed.

Fuel Properties of Ethanol

About 1 billion gallons of fuel ethanol are produced from corn in the United States, the equivalent of 0.08 quad. The corn ethanol produced is blended at 10% with about 9% of the gasoline consumed. Because corn is grown domestically, ethanol use reduces the balance-of-payments deficits for imports of fuels while providing a secure source of transportation fuel.

Ethanol blends cause engines set for gasoline to run lean, and blends reduce carbon monoxide emissions by 10% to 30% (U.S. Department of Agriculture 1987; Livo et al. 1989; Johnson 1989; Watson 1988). In addition to 10% blends, ethanol can be reacted with isobutylene to form ethyl tert-butyl ether (ETBE) for blending with gasoline (Pahl 1988; Anderson 1988). If ETBE is blended at 22% with gasoline, the amount of ethanol used is equivalent to that for 10% blends, and ETBE in gasoline also reduces carbon monoxide emissions. As an added benefit, ETBE lowers the Reid vapor pressure of gasoline, thereby decreasing the release of smog-forming compounds. Alternatively, ethanol can be employed directly as a neat (close to 100%) fuel. Use of neat ethanol reduces smog formation because the lower volatility of neat ethanol reduces emissions, the photochemical reactivity of ethanol and its combustion products is low, and the amount of nitrogen oxides can be less because of reduced flame temperatures (U.S. Environmental Protection Agency 1987; Browning et al. 1981; Risch 1988; U.S. Department of Energy 1978; Wilson 1987).

As shown in Table 1, ethanol has many fuel properties that are desirable. Blends of ethanol or ETBE with gasoline increase the octane of the mixture and can improve the performance. Neat ethanol provides superior efficiency and performance to gasoline because it requires lower stoichiometric air/fuel ratios, has a higher latent heat of vaporization, provides higher octane values, and has a lower flame temperature. Thus, ethanol and methanol are often preferred to gasoline for high performance in automobile races such as the Indianapolis 500. The fact that the majority of new cars in Brazil have been run on pure ethanol clearly shows that it is a suitable fuel.

When blended with gasoline at the 10% ethanol level as a direct blend or at equivalent levels through use of ETBE, the current potential market for ethanol is about 11 billion gallons or 1.3 quads. For use as a neat fuel, about 140 billion gallons of ethanol would displace the existing gasoline consumption of 112 billion gallons (13 quads), because ethanol can provide approximately 80% of the mileage of gasoline on a volumetric basis (Browning et al. 1981; Risch 1988; U.S. Department of Energy 1978; Wilson 1987; Bernhardt 1978; Kampen 1988). An additional market of 8 billion gallons of ethanol is potentially available for use as a solvent and as a feedstock for production of ethylene and other chemicals (Busche 1985).

Biomass Feedstock Options

Ethanol can be produced from several carbohydrate-containing feedstocks including sugar, corn starch, and cellulosic biomass. Processes for utilizing these substrates are in various stages of technical maturity. Processes for sugar and corn conversion are practiced commercially; processes for cellulosic biomass utilization are still under development in this country. Although ethanol is also made from ethylene, that technology does not address some of the critical issues that warrant fuel ethanol production in the first place and has been displaced by fermentation ethanol for fuel use (*Chemical Marketing Reporter* 1985). Thus, the focus of this discussion will be on fermentation ethanol.

Sugar Cane

About 4.0 billion gallons of ethanol are produced annually in Brazil from sugar cane (J.E. Sinor Consultants 1990). For a time, the majority of new cars in that country ran on neat ethanol, while the remainder operated on 20% ethanol - 80% gasoline blends (*New Fuels Report* 1990a). However, the price of ethanol in Brazil is higher than for gasoline; ethanol is subsidized by taxes on gasoline to promote its use as a fuel. Furthermore, because sugar is primarily used as food, rising world sugar prices have resulted in shortages of sugar for ethanol production at times. Extensive news coverage has resulted from these problems and related problems that Brazil has experienced with the substitution of ethanol derived from sugar cane for gasoline (*New Fuels Report* 1990a; *New Fuels Report* 1990b; Kandell 1989; Anderson 1990), but Brazil is once again aggressively pursuing ethanol production from sugar cane. In the United States, sugar prices are typically controlled at more than $360/ton, and ethanol would have to sell at a price of more than $2.30/gal at the plant gate just to recover the cost of sugar. Because this is well above current wholesale gasoline prices of about $0.55 to $0.75/gal, fermentation of sugar to ethanol is not a competitive technology in this country.

Table 1. Properties of Ethanol, ETBE, Isooctane, and Gasoline

Property	Ethanol	ETBE	Isooctane	Unleaded Regular Gasoline
Formula	C_2H_5OH	$(CH_3)_3COC_2H_5$	C_8H_{18}	C_4 to C_{12}
Molecular weight	46.07	102.18	114	--
Density, lb/gal @ 60°F	6.61	6.26	5.75	6.0-6.5
Air/fuel stoichiometry (moles)	14.32	42.9	59.68	57.28
Lower heating value (Btu/gal)	76,000	96,900	109,900	109,000-119,000
Energy, Btu/ft^3 of standard stoichiometric mixture	98.4	100	98.9	
Octane number				
RON	106	118	100	91-93
MON	89	102	100	82-84
(RON+MON)/2	98	110	100	88
Blending RON	118-141[a]	117-120[b]		
Blending MON	86-97[a]	101-104[b]		
(Average blending RON+MON)/2	111	111		
Latent heat of vaporization Btu/gal @ 60°F	2,378	--	812	~900
Boiling Temperature, °F	172	158	257	80-437
Reid vapor pressure, psi				
pure component	2.3	4.4		
blending	12-27	3-5		8-15
Water solubility, %				
fuel in water	100	2.0	negligible	negligible
water in fuel	100	0.6	negligible	negligible

[a] 10% blends
[b] Assumed 12.7% blend

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Corn and Other Starch Crops

In the United States, nearly 400 million bushels of corn are used each year to produce almost 1 billion gallons of anhydrous ethanol for 10% blends with gasoline. Ethanol from corn sells for about $1.20 to $1.30/gal. The U.S. Department of Agriculture has estimated that approximately 4 to 5 billion additional gallons of ethanol could be produced from 1.6 billion bushels of corn in the United States before agricultural resources would be taxed and strong upward pressure exerted on grain prices (U.S. Department of Agriculture 1989). Thus, corn provides a valuable source of ethanol.

Cellulosic Biomass

Cellulosic biomass is a complex mixture of carbohydrate polymers from plant cell walls known as cellulose and hemicellulose, plus lignin and a small amount of other compounds known as extractives, as shown in Figure 1. Examples include agricultural and forestry residues, municipal solid waste (MSW), herbaceous and woody plants, and underutilized standing forests. Cellulosic biomass is low in cost because it is inexpensive to produce. The cellulose fraction is composed of glucose sugar molecules bonded together in long chains that are held together in a crystalline structure. The hemicellulose portion of biomass is made of long chains of a number of different sugars and does not have a crystalline structure. For hardwoods, the predominant component of hemicellulose is xylose, a five-carbon sugar that has historically been more difficult to convert into useful products than has glucose.

For the United States, it is estimated that the total amount of underutilized wood, agricultural residues, short-rotation energy crops, and MSW could provide about 2700 million dry tons of cellulosic biomass per year at prices from $20 to $70 per dry ton (Lynd 1989). This quantity of feedstock can generate about 300 billion gallons of ethanol, more than enough to meet the total current gasoline market in the United States of 140 billion gallons of ethanol equivalent twice over. The price of these raw materials is also low enough to provide a reasonable margin for conversion into ethanol. Even though these values are subject to significant uncertainty, they indicate that the resource base of renewable feedstocks is substantial while the cost is reasonable. Thus, cellulosic biomass is a favorable feedstock for fuel ethanol production.

Ultimately, abundant feedstocks are required to achieve large-scale ethanol production. Thus, the Oak Ridge National Laboratory (ORNL) manages a Biomass Production Program for DOE to develop technology for producing fast-growing herbaceous and woody crops that will provide an abundant and low-cost substrate for ethanol production. Energy crops developed by ORNL will be essential to widespread ethanol use.

Conversion of Cellulosic Biomass into Ethanol

Cellulosic biomass is an inexpensive feedstock, and acids or enzymes will catalyze the breakdown of the cellulose and hemicellulose chains into their component sugar molecules, which can be fermented into ethanol. Lignin is a complex phenolic polymer that cannot be fermented into ethanol. The challenge is to develop low-cost methods to convert the naturally resistant cellulose and hemicellulose into ethanol.

Over the years, a number of processes have been studied for conversion of cellulose-containing biomass into ethanol catalyzed by dilute acid, concentrated acid, or enzymes known as cellulases. In each of these
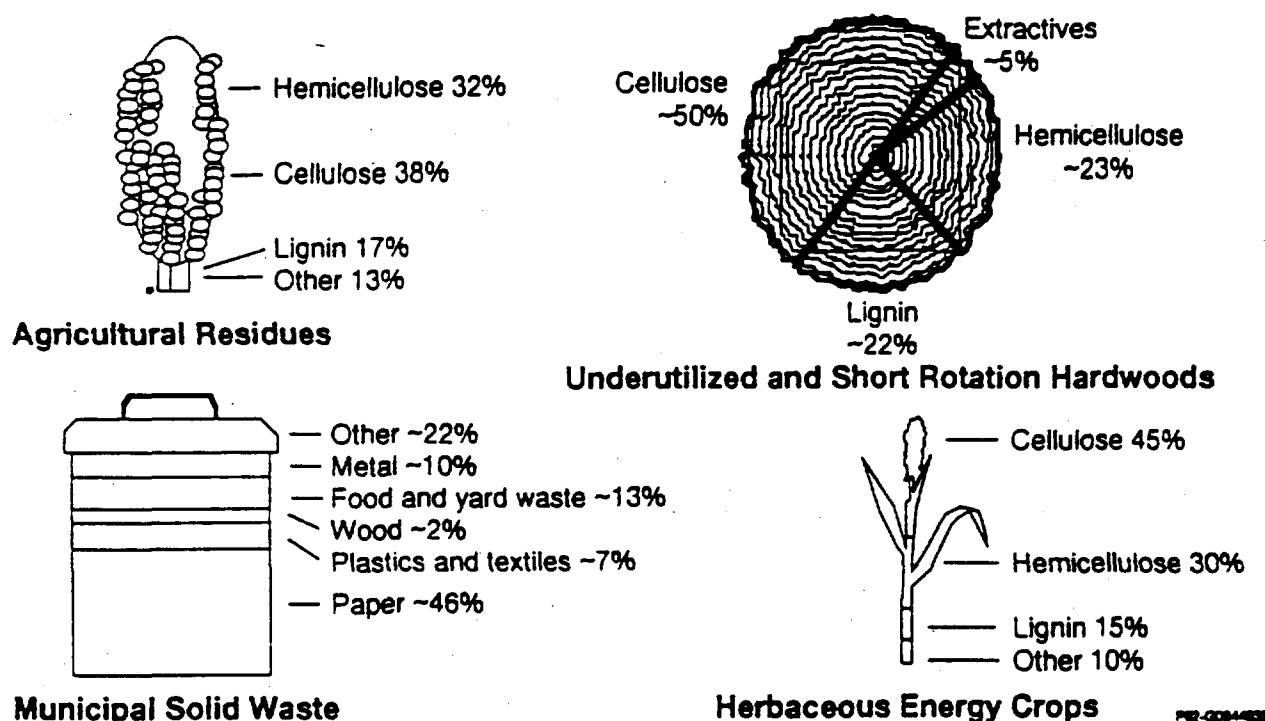
Agricultural Residues
- Hemicellulose 32%
- Cellulose 38%
- Lignin 17%
- Other 13%

Underutilized and Short Rotation Hardwoods
- Cellulose ~50%
- Extractives ~5%
- Hemicellulose ~23%
- Lignin ~22%

Municipal Solid Waste
- Other ~22%
- Metal ~10%
- Food and yard waste ~13%
- Wood ~2%
- Plastics and textiles ~7%
- Paper ~46%

Herbaceous Energy Crops
- Cellulose 45%
- Hemicellulose 30%
- Lignin 15%
- Other 10%

Figure 1. Cellulosic biomass consists of cellulose, hemicellulose, lignin, and some extractives as shown here for representative examples of agricultural residues (corn cobs), hardwood, municipal solid waste, and herbaceous plants.

options, the feedstock is pretreated to reduce its size and open up the structure as shown in Figure 2. The cellulose fraction is hydrolyzed by acids or enzymes to produce glucose sugar, which is subsequently fermented to ethanol. The soluble xylose sugars derived from hemicellulose are also fermented to ethanol, and the lignin fraction can be burned as fuel to power the rest of the process, converted into octane boosters, or used as a feedstock for the production of chemicals.

Acid-Catalyzed Processes

Several dilute acid hydrolysis pilot plants were constructed in the United States during war time as part of an effort to produce ethanol for fuel use (Wenzl 1970), but the economics were too unfavorable to allow continued operation in a free market economy. Dilute acid-catalyzed processes are currently operated in the Soviet Union for converting cellulosic biomass into ethanol and single cell protein. Thus, acid-catalyzed processes provide a near-term technology for production of fuel-grade ethanol from cellulosic biomass, but the low yields of 50% to 70% typical of dilute acid systems make these processes unable to compete with existing fuel options (Wright 1983; Wright 1988a). Concentrated sulfuric or halogen acid options achieve the high yields required. However, because low-cost acids (e.g., sulfuric) must be used in large amounts while more potent halogen acids are relatively expensive, recycling of acid by efficient, low-cost recovery operations is essential to achieve economic operation (Wright and Power 1985a; Wright et al. 1985b). Unfortunately, the acids must also be recovered at a cost substantially lower than that of producing these inexpensive materials in the first place—a difficult requirement.
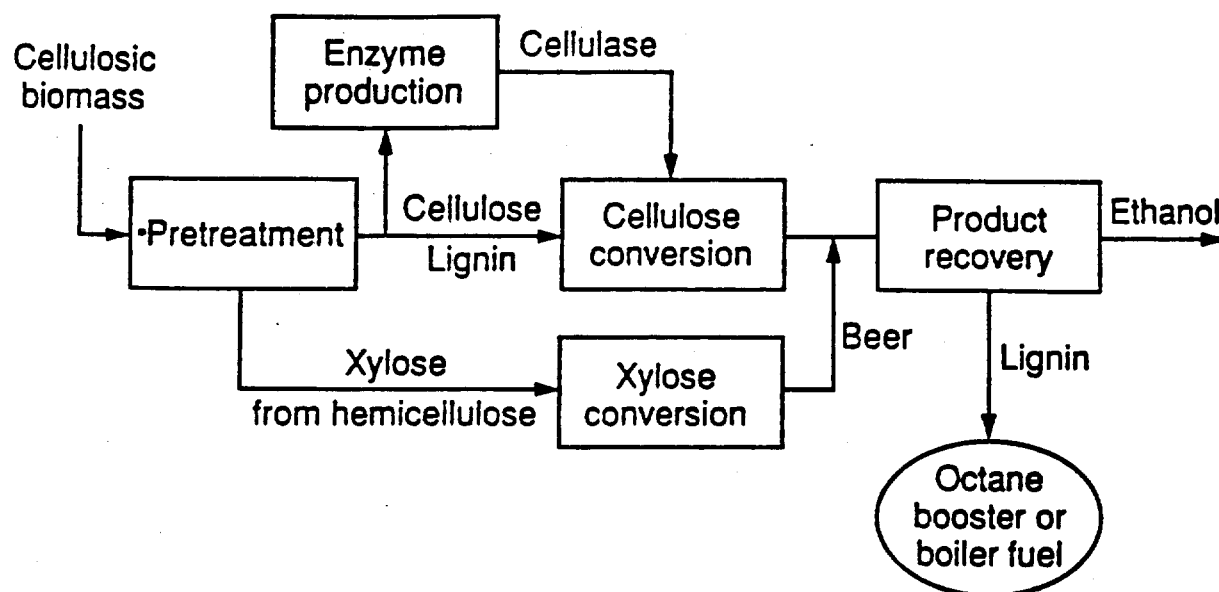
Figure 2. The process flow diagram for acid- or enzyme-catalyzed conversion of cellulosic biomass to ethanol.

Enzyme-Catalyzed Processes

Enzyme-catalyzed processes achieve high yields under mild conditions with relatively low amounts of catalyst. Enzymes are also biodegradable and environmentally benign. Over the years, several enzyme-based processes have been studied at the laboratory scale, but only a few investigations have been expanded to a larger scale. The processes considered are discussed below.

Separate Hydrolysis and Fermentation

In the separate hydrolysis and fermentation (SHF) process, the cellulosic biomass is first processed in a pretreatment device to open the biomass structure and facilitate subsequent processing. A portion of the pretreated biomass is used in an enzyme production vessel to support growth of a fungus that produces cellulase enzyme, and the cellulase enzyme is added to the bulk of the pretreated substrate in a hydrolysis reactor. At this stage, the enzymes catalyze the breakdown of the cellulose by the so-called hydrolysis reaction to form glucose sugar. The stream from the hydrolysis process passes on to a fermenter to which yeast are added to convert the glucose into ethanol. Finally, the ethanol is separated from the rest of the fermentation broth in a purification step (Mandels et al. 1974; Wilke et al. 1976).

Simultaneous Saccharification and Fermentation

The sequence of steps for the simultaneous saccharification and fermentation (SSF) process is virtually the same as for separate hydrolysis and fermentation except that hydrolysis and fermentation are combined in one vessel (Gauss et al. 1976; Takagi et al. 1977). The presence of yeast along with the enzymes

minimizes accumulation of sugar in the vessel, and because the sugar produced during breakdown of the cellulose slows down the action of the cellulase enzymes, higher rates and yields are possible for SSF than for SHF. Additional benefits are that one of the expensive fermentation vessels is eliminated and that the presence of ethanol makes the fermentation mixture less vulnerable to invasion by unwanted microorganisms.

Direct Microbial Conversion

The direct microbial conversion process combines the enzyme production, cellulose hydrolysis, and sugar fermentation steps in one vessel (Veldhuis et al. 1936; Ng et al. 1977; Cooney et al. 1978). In the most extensively tested configuration, two bacteria are employed that produce cellulase enzymes and ferment the sugars formed by breakdown of cellulose and hemicellulose into ethanol. Unfortunately, the bacteria also produce a number of products in addition to ethanol, and yields are lower than for the SHF or SSF processes.

Although the cost of cellulosic biomass is low enough to provide a reasonable margin for profitable conversion into ethanol, evaluations of acid-catalyzed options for converting cellulosic biomass into ethanol have shown that the ethanol yields from these processes are too low, while concentrated acid options require acid recovery at lower costs than are now feasible. On the other hand, the enzyme-catalyzed options provide high yields of ethanol with low concentrations of enzyme. In addition, although the price of ethanol produced from some enzyme- and acid-catalyzed processes may be similar to each other now, enzyme-catalyzed processes have tremendous potential for technology improvements that could bring the selling price of ethanol down to levels competitive with existing fuels (Wright 1988a; Wright 1988b). In particular, NREL has focused on the SSF process as a promising route to achieve low-cost fuel ethanol production within a reasonable time frame (Wright et al. 1988c). As shown in Figure 3, the SSF process combines the enzymatic hydrolysis of cellulose and fermentation of the glucose sugars produced in one vessel to speed rates while reducing equipment costs.

Pretreatment of Cellulosic Biomass

Cellulosic biomass is naturally resistant to enzymatic attack, and a pretreatment step is required to overcome this resistance if the enzyme-catalyzed hydrolysis process is to proceed at a reasonable rate with the high yields vital to economic viability. Several options have been considered for biomass pretreatment including steam explosion, acid-catalyzed steam explosion, organosolv, and dilute acid. At this time, the dilute acid option appears to have the best near-term economic potential (Wright 1988b). In this process, about 0.5% sulfuric acid is added to the feedstock, and the mixture is heated to about 140° to 160°C for 5 to 20 min. Under these conditions, most of the hemicellulose is broken down to form xylose sugars, leaving a porous material of primarily cellulose and lignin that is more accessible for enzymatic attack. Evaluation of the dilute acid process with various agricultural residues, short-rotation hardwoods, and herbaceous energy crops has consistently shown that the conversion yields correlate well with the degree of hemicellulose removal (Torget et al. 1990). Although this process has good near-term potential, significant benefit would result if a low-cost scheme could be devised that would also remove lignin, because the solid lignin associated with the cellulose creates some processing difficulties in the fermentation step.
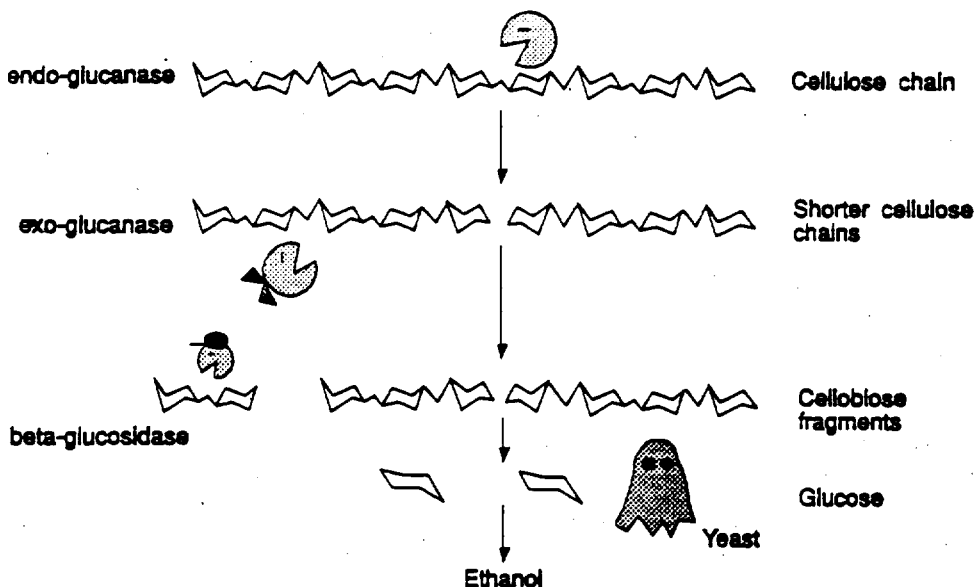
Figure 3. The simultaneous saccharification and fermentation (SSF) process combines cellulose breakdown into glucose by cellulase enzymes (endo- and exo-glucanase plus beta-glucosidase) with fermentation of glucose into ethanol to speed rates and lower costs.

Hemicellulose Utilization

The hemicellulose polymers in cellulosic biomass such as hardwood, agricultural residues, and herbaceous plants can be readily broken down to form the five-carbon sugar xylose during the pretreatment step. However, until recently, the xylose stream could not be utilized, and it was necessary to send this material to waste disposal. From an economic perspective, this costs the process twice: first, because we paid for the xylose, it is costly to throw it away; and second, the cost of waste disposal inflicts a large penalty on the process.

Several options, outlined below, have been examined for xylose utilization.

Conversion of Xylose into Furfural

For dilute acid-catalyzed breakdown of cellulose to fermentation sugars, a significant fraction of the xylose will degrade into furfural (Wright 1983). Similarly, the xylose released by pretreatment can also be reacted to furfural. This product is currently manufactured for use in foundry and other applications, so it could be sold as a by-product, generating additional revenues. However, the furfural market would be quickly saturated by the volume of furfural that would accompany large-scale application of ethanol as a fuel (Gaines and Karpuk 1986). Thus, although furfural sales could provide a valuable role in initial

introduction of a few ethanol plants, the sales would not support the commercialization of a large-scale ethanol production capability.

Yeast for Ethanol Production

Another avenue is to use certain strains of yeast that are known to ferment xylose into ethanol, such as *Candida shehatae, Pichia stipitis, and Pachysolen tannophilus* (Jeffries et al. 1985; Gong et al. 1981; Beck et al. 1990; Jeffries 1989). However, these strains require small amounts of oxygen in the fermentation broth to ferment xylose. Unfortunately, large-scale production of ethanol fuels will probably require the use of huge fermenters with volumes approaching a million gallons each, and proper control of oxygen in such large vessels could be virtually impossible. Furthermore, these yeast strains typically cannot yet achieve very high ethanol yields or rates or tolerate high ethanol concentrations (Hinman et al. 1989).

Other Microorganisms for Ethanol Production

Other microorganisms, such as thermophilic bacteria and fungi, can anaerobically ferment xylose into ethanol (Lynd 1989; Buchert et al. 1989; Antonopoulos and Wene 1987; Asther and Khan 1984; Alexander et al. 1981; Slapack et al. 1987). However, ethanol tolerance has not been satisfactorily demonstrated for bacteria, although some new evidence suggests that previous conclusions may have been premature (Lynd 1991). Similarly, historic data suggest that ethanol yields are low. However, new information indicates that the yields could be improved in continuous culture (Lynd 1991). The fungi evaluated currently suffer from similar limitations in both ethanol tolerance and yield.

Simultaneous Fermentation and Isomerization of Xylose to Ethanol

Several groups have studied the use of xylose isomerase enzyme to convert xylose into an isomer called xyiulose that many yeast can ferment into ethanol under anaerobic conditions (Jeffries 1981; Chaing et al. 1981). Recently, researchers at NREL have genetically engineered the common bacteria *Escherichia coli* to produce large quantities of xylose isomerase for such a process, and ethanol yields of 70% of theoretical have been achieved in the simultaneous fermentation and isomerization of xylose (SFIX) process (Lastick et al. 1990). In this configuration, the enzyme and yeast are employed together to drive the equilibrium limited fermentation to completion, with the primary yield loss resulting from xylitol formation (Lastick et al. 1990; Tewari et al. 1985). The SFIX process has the advantage of employing anaerobic yeast that are easier to use on a large scale, but the need to provide xylose isomerase enzyme and adjust for differences in pH optima between the yeast and enzyme complicate the technology.

Genetically Altered *E. coli*

Researchers at the University of Florida have successfully introduced the genes from *Zymomonas mobilis* into the common bacteria *E. coli* as well as other bacteria so that the latter can now ferment xylose directly into ethanol (Ingram and Conway 1988; Ingram et al. 1987). This approach has the advantage that a single organism can carry out the fermentation of xylose, and initial data suggest that high yields are possible. However, *E. coli* requires operation at near-neutral pH while production of by-product acids tends to drive the pH down, thus requiring addition of bases to control the pH. Invasion by other bacteria may also be problematic.

At this time, the most promising option for xylose conversion is the use of genetically engineered *E. coli* followed by the SFIX system. However, full integration of these technologies into the overall conversion process is required to evaluate and improve their performance. Advantages would also result if the limitations of these options could be overcome by further genetic modifications or other approaches.

Lignin Conversion

As shown in Figure 1, lignin generally represents the third largest fraction of cellulosic biomass and is not significantly different in quantity than hemicellulose. Thus, it is important to derive value from the lignin fraction if the economic goals of the Ethanol from Biomass Program are to be achieved. Three options, discussed below, lead the possibilities for lignin use.

Using Lignin as a Boiler Fuel

Lignin has a high energy content and can be used as a boiler fuel (Wright 1988a; Hinman et al. 1989; Domalski et al. 1987). The amount of lignin in most feedstocks is more than enough to supply all the heat required for the pretreatment, enzyme production, cellulose conversion, and xylose fermentation step, and to generate enough electricity to meet the electrical demands of these processes. In fact, excess electricity beyond all of these needs is generated, and additional revenue can be generated from electricity exports from the plant. The electricity sold for current plant designs is equivalent to about 10% of the Btu value of the ethanol product, and greater revenues are likely as the technology is improved to require less process heat and electricity.

Producing Octane Boosters from Lignin

Lignin is a complex phenolic polymer that can be broken down to form a mixture of monomeric phenolic compounds and hydrocarbons. The phenolic fraction can be reacted with alcohols to form methyl or ethyl aryl ethers, which are good oxygenated octane boosters (Johnson et al. 1990). Because octane boosters are more valuable than boiler fuel, this option for lignin use would generate more revenue. However, the technology must be improved to provide high product yields, and the conversion costs must be very low to provide a net income gain for the ethanol plant.

Producing Chemicals from Lignin

A number of chemicals could be produced from lignin including phenolic compounds, aromatics, dibasic acids, and olefins (Busche 1985). Such materials could have a high value that would augment the total revenue for the ethanol plant. However, just as for the conversion of lignin into octane boosters, the cost of the conversion process must be low enough to ensure a net gain in revenue. In addition, high yields of target products will likely be necessary to achieve economic viability.

Progress and Potential for Improvement

Progress on the enzyme-catalyzed processes to convert cellulosic biomass into fuel ethanol has been substantial during the last 10 years, with projected selling prices dropping from about $3.60/gal in 1980 (Wright 1988a) to only about $1.27/gal now (Chem Systems 1990). This reduction in selling price is caused by improved rates and yields from the SSF process, improvements in enzymes to achieve high yields with lower loadings, proper selection of the fermentative microbes, and advances in xylose fermentations through genetic engineering.

Although research progress has been substantial, significant opportunities still exist to lower the selling price of ethanol from cellulosic biomass to $0.67/gal at the plant gate. Key target areas include further improvements in glucose and xylose yields from pretreatment, increased ethanol yields to 90% or greater from cellulose and xylose fermentations, decreased stirring and pretreatment power requirements, better productivities through continuous processing and biocatalyst immobilization, low-cost production of octane enhancers or chemicals from lignin, increased ethanol concentration, and reduction of fermentation times. Because feedstock costs are a significant fraction of the final product selling price, improvements in feedstock production, collection, and genetics could provide additional cost reductions through economies of scale for larger ethanol plants, decreased feedstock costs, and less nonfermentable feedstock. Many of these goals have been met individually; the evidence that the rest can be achieved is great. The primary need is to meet these goals simultaneously. It is also encouraging that enough options exist to lower the selling price of ethanol that not all the technical goals must be achieved to reach the target selling price.

Applications to Corn Ethanol Production

The cost of the feedstock is an important portion of the projected selling price of ethanol from cellulosic biomass. At the current $1.27/gal selling price, $0.46 is for feedstock at a price of $42/ton delivered to the plant gate. Figure 4 illustrates how the price of ethanol changes with the cost of the feedstock used. For example, if a free feedstock could be obtained, ethanol could be produced for about $0.81/gal. Because ethanol from corn now sells for about $1.20 to $1.30/gal, use of an inexpensive feedstock could make the process cost-competitive now. Several possible low-value or waste streams could prove attractive, including the carbohydrate fractions of corn gluten feed from corn wet milling; and distillers' dried grains and solubles (DDGS) from dry milling of corn; agricultural waste streams such as corn cobs, corn stover, or wheat straw; commercial processing waste streams such as white water in paper manufacture; and domestic wastes such as wastepaper and MSW. Although such feedstocks are of limited availability, they provide an opportunity to establish the technology early.

Utilization of the Fiber in the Wet Milling Process

About two-thirds of the ethanol made from starch in the United States is made by the wet milling process. Typically 2.5 gal of ethanol, 13 lb of an animal feed coproduct called corn gluten feed, 3 lb of another animal feed coproduct called corn gluten meal, and 1.7 lb of corn oil are produced from a bushel of corn (47.3 lb dry weight). Corn gluten feed, an animal feed containing 21% protein, results from combining three by-product streams: fiber, germ meal, and corn steep liquor. The price of corn gluten feed and other animal feeds seems to be set largely by their protein content, as shown in Figure 5, giving less value to the cellulose, hemicellulose, and other carbohydrate materials. In fact, since most of the corn gluten feed is sold to the European Economic Community (EEC), the cellulose, hemicellulose, and other carbohydrate materials add to shipping costs. A process that could convert the cellulose, hemicellulose,

and other carbohydrates into valuable products such as ethanol could enhance the revenue for the plant while lowering the costs of shipping the corn gluten feed to the EEC.

The fiber and germ meal product streams contain significant amounts of cellulose, hemicellulose, and starch. The composition of the fiber stream is about 22.5% starch, 12.5% protein, 3% fat, 10% cellulose, 30% hemicellulose (mostly xylan), 0.5% lignin, and 2% ash. The germ meal contains 26% protein, 20% starch, 5% fat, 13% cellulose, 32% hemicellulose (mostly xylan), 1% lignin, and 4% ash. From every bushel of corn, 5.4 lb of fiber and 1.9 lb of germ meal product are produced. Thus, from one bushel of corn, these combined streams contain 2.2 lb of hemicellulose, 0.79 lb of cellulose, and 1.0 lb of starch. In terms of ethanol, this represents 0.26 gal of ethanol from hemicellulose and cellulose, and 0.13 gal of ethanol from starch, or a total of 0.39 gal of ethanol, an increase of 16% over the quantity of ethanol typically produced from a bushel of corn. This increased production would increase ethanol revenue by 16% while decreasing shipping costs of corn gluten feed by as much as 42%. For every 1 billion bushels of corn processed, total ethanol production from the carbohydrate fraction of the fiber and germ meal streams could be 400 million gallons, which represents revenues of $480 million at an ethanol price of about $1.20/gal.

On the other hand, the protein content of the corn gluten would be higher after removal of the fiber. As a result, revenues from protein sales could remain the same if the product is valued by its protein content and while shipping costs of the corn gluten feed could drop by as much as 42%. Other products besides ethanol could be considered, and use of the oil content of the fiber stream and germ meal may also be worth considering.

Utilization of the Carbohydrates in DDGS for the Dry Milling Process

The remaining ethanol made in the United States is from the dry milling of corn. In this process, 2.5 to 2.6 gal of ethanol are produced per bushel of corn processed, along with about 17 lb of an animal feed coproduct called DDGS, and 17 lb of carbon dioxide. DDGS contains at least 27% protein, and as shown in Figure 5, the price of DDGS seems to be set largely by its protein content, giving little value to the cellulose and hemicellulose. In fact, these carbohydrates add to shipping costs. As for wet milling, a process that converts the cellulose and hemicellulose into a valuable product such as ethanol could enhance revenues for the plant while lowering shipping costs.

Essentially all the cellulose and hemicellulose from corn ends up in the DDGS product, along with some starch. Because the cellulose and hemicellulose comprise 9.5% of the dry weight of corn, 4.3 lb of these materials are expected in 17 lb of DDGS from one bushel of corn. If converted into ethanol, the hemicellulose and cellulose in DDGS could yield 0.37 gal of ethanol from every bushel of corn processed. This is an increase of 14% to 15% over the ethanol typically produced from a bushel of corn. Sale of this increase would raise ethanol revenues 14% to 15% while possibly maintaining animal feed coproduct revenues as a higher value protein feed and decreasing shipping costs by as much as 25%. For every 100 million bushels of corn processed, total ethanol production from the hemicellulose and cellulose content of DDGS could be 37 million gallons. Other products besides ethanol could be considered, and use of the oil content may also be worth considering.
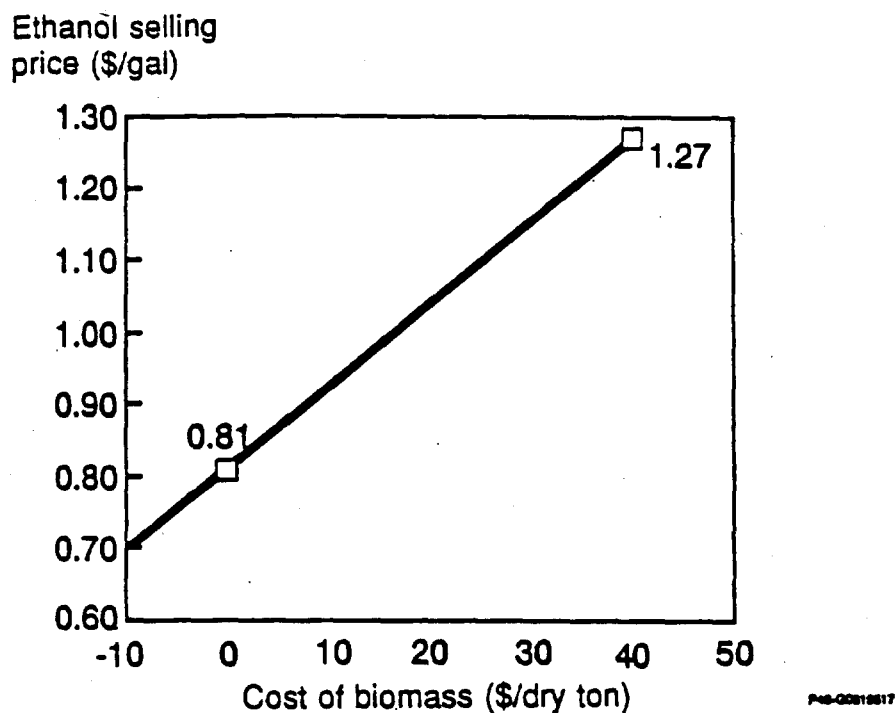
Ethanol selling
price ($/gal)

Figure 4. The current price to ethanol from cellulosic biomass is $1.27/gal when the cost of the feedstock is $42/ton. Lower cost feedstocks result in a lower cost of ethanol production, as shown here.
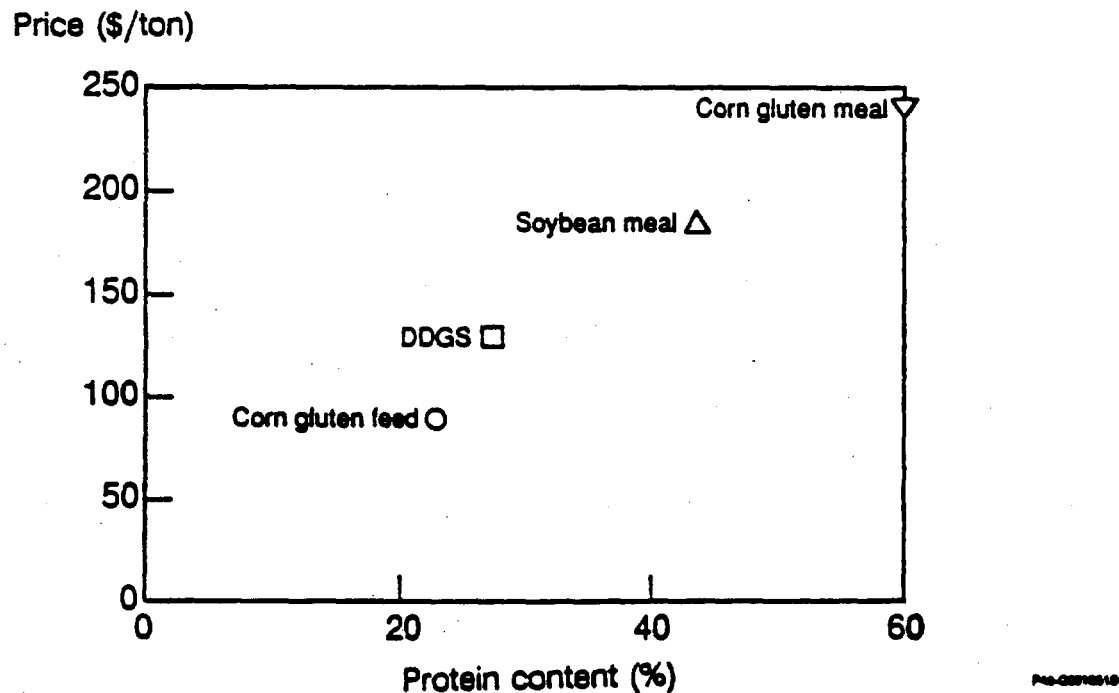
Price ($/ton)

Figure 5. Relationship among the market prices of various animal feeds and their protein content, based on recently reported prices.

Global Climate Change

The carbon dioxide released during ethanol fermentation and combustion is recycled back to grow new biomass, which replenishes that harvested for ethanol manufacture. In addition, the lignin in the feedstock can be burned to provide all of the process heat and electricity needed to drive the conversion process, and some electricity is left to sell for added revenue. Thus, as illustrated in Figure 6, carbon dioxide actually provides the key link between the fuel and the biomass resource; it does not accumulate in the atmosphere as a result of either conversion or utilization (Wyman and Hinman 1990; Lynd 1990). Of course, new trees or other biomass must be planted to replace those harvested for energy, just as is done in the agricultural, paper, and forest products industries. As an added benefit, growth and harvesting of cellulosic feedstocks require far less fertilizer and cultivation than growth and harvesting of food crops, thereby reducing the fossil fuel requirements for biomass production. Although some argue that the use of coal, natural gas, and petroleum in ethanol production from corn negates some of the benefits with respect to global climate change (Ho 1989; Segal 1989), these conclusions are heavily swayed by the high use of coal to provide process heat and electricity for ethanol production from corn; the use of lignin as a boiler fuel negates this major carbon dioxide contribution. Furthermore, biomass, methane from biomass, and neat ethanol could be substituted directly for fossil fuels in the cultivation and harvesting of cellulosic biomass, maintaining the carbon dioxide balance.
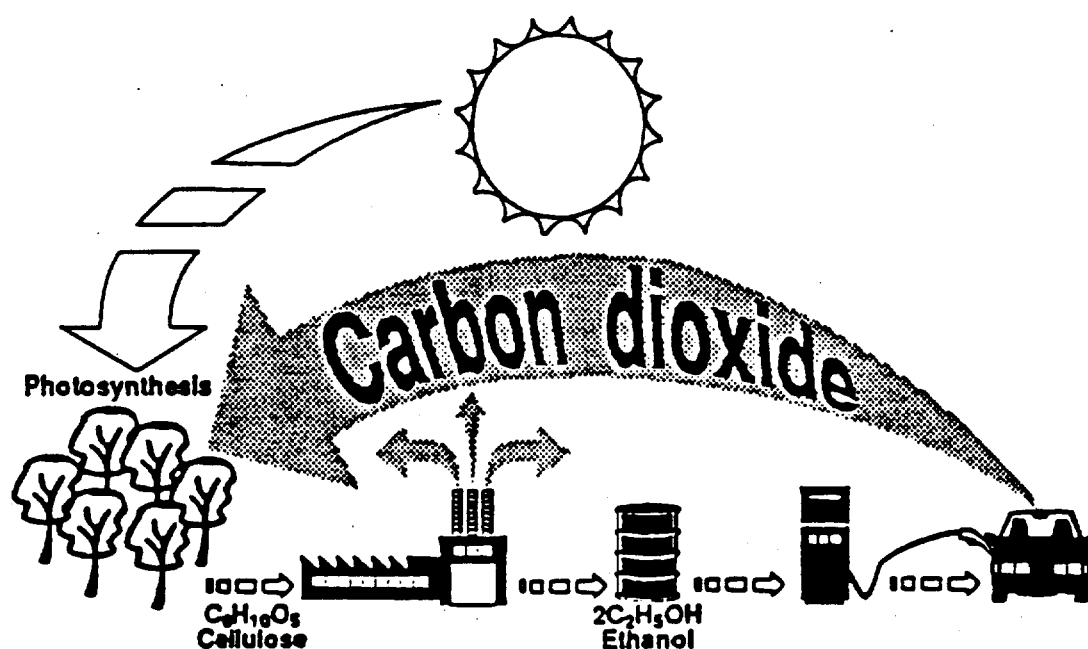

Figure 6. For production of ethanol from cellulosic biomass, the carbon dioxide released in the fermentation step and during ethanol combustion is recycled to grow new plants to replenish those harvested as feedstock. Because the lignin in the biomass can be burned as boiler fuel to provide all the energy needed to run the overall process, no fossil fuel is required in the process, and ethanol production and use contributes no net accumulation of carbon dioxide to the atmosphere.

Conclusions

Ethanol is a clean-burning, high-octane fuel that can be used in today's transportation sector. Enough ethanol could be made from cellulosic biomass within the United States to replace gasoline consumption. This means that using ethanol derived from biomass such as agricultural and forestry wastes would reduce the strategic vulnerability of the United States, prevent sudden changes in price, and lower our trade deficit for imports. When blended with gasoline, ethanol or the oxygenate ETBE derived from ethanol reduces emissions of carbon monoxide and unburned hydrocarbons. "Pure" ethanol reduces the release of smog-forming compounds. The carbon dioxide released during ethanol production and use can be recaptured by plants to replenish the biomass supply, so ethanol does not contribute to the accumulation of carbon dioxide in the atmosphere and the potential for global climate change because of the "greenhouse effect."

Both acid- and enzyme-catalyzed reactions have been evaluated for conversion of cellulosic biomass into ethanol, and research has been focused on enzymatic hydrolysis technology because of its potential to achieve high yields of ethanol under mild conditions. In particular, the SSF process is favored for ethanol production from the major cellulose fraction of the feedstock because of its low cost potential. Technology has also been developed for converting the second largest fraction, hemicellulose, into ethanol, and the remaining lignin can be burned as boiler fuel to power the conversion process and generate extra electricity to export. Together, developments in conversion technology have reduced the selling price of ethanol from about $3.60/gal 10 years ago to only $1.27/gal now. Additional technical targets have been identified to bring the selling price down to about $0.67/gal with an aggressive research and development program.

Technology for conversion of cellulosic biomass to ethanol could be applied to both existing wet and dry milling processes to substantially enhance ethanol revenues, while maintaining revenues from the sale of animal feed coproducts with higher protein content. Because the carbohydrates in these products have little apparent value, the application of cellulose conversion technology to these processes could result in lower ethanol costs for the plant. Other low-cost materials could also be converted into ethanol at prices competitive in today's fuel market.

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